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TITLE AUTOMATIC TITRATOR FOR HIGH PRECISION PLUTONIUM ASSAY

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AUTOMATIC TITRATOR FOR HIGH PRECISION PLUTONIUM ASSAY

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Abstract

Highly precise assay of plutonium metal is required for accountability measurements. We have developed an automatic titrator for this determination which eliminates analyst bias and requires much less analyst time. The analyst is only required to enter sample data and start the titration. The automated instrument titrates the sample, locates the end point, and outputs the results as a paper tape print-out. Precision of the titration is less than 0.03% relative standard deviation for a single determination at the 250-mg plutonium level. The titration time is less than 5 min.

The Analytical Chemistry Group of Los Alamos National Laboratory must analyze a large number of plutonium metal samples with high precision for accountability measurements and for characterization of source material used to prepare standard reference materials. It is essential that the assay method be precise and desirable and that it be rapid and free of analyst bias. The method currently in use at Los Alamos National Laboratory is based on the method of Caldwell [1] and coworkers and has been successfully used for over twenty years.

The method has relatively few operations. A 250$\pm$25 mg sample of plutonium metal is dissolved in hydrochloric acid producing primarily Pu(III). The solution is flowed through a lead reductor column into a beaker containing 5 mL 9$\underline{M}$ H_2SO_4 and 200 μl ferroin indicator. The column is rinsed with approximately 100 mL 0.1$\underline{M}$ HCl to completely transfer all the sample and the Pu(III) is titrated with 0.05 meq ceric bisulfate/g to a photometric end point using a weight buret. The photometer used to monitor the titration for detection of the ferroin end point is based on a design described by Rost [2].

Using a weight buret an experienced analyst can attain a precision of 0.03% relative standard deviation for a single determination. Use of a weight buret is slow and particularly tedious in glove box operation. Calculating an estimated volume required for each titration allows the analyst to rapidly deliver the bulk of the titrant. This reduces the time required for the titration, but also introduces the possibility of the estimate influencing the result.

To reduce the tedium and eliminate analyst bias, we have developed an automatic titrator for performing the titration. The analyst prepares the samples as usual and starts the titrator. The instrument titrates the sample, locates the end point, and outputs the results as a paper tape print-out. The automated titrator eliminates analyst bias and requires much less analyst time freeing them for other tasks such as sample preparation. The analyst can be preparing the next sample while the automated titrator is carrying out a titration.

The automated titrator uses a Hewlett-Packard HP-85 computer as a controller, a Metrohm 655 Dosimat Automatic Buret to deliver the titrant, and a Brinkmann Probe Colorimeter to monitor the color change of the solution to locate the end point. For minimum disturbance to the existing operations, no changes were made to the method other than automating the titration.

The relatively inexpensive HP-85 is a powerful computer and a good controller. It is small, an advantage because of limited space in the laboratory, and contains the display, estimated volume required for each titration allows the analyst to rapidly deliver the bulk of the titrant. This reduces the time required for the titration, but also introduces the possibility of the estimate influencing the result.

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The relatively inexpensive HP-85 is a powerful computer and a good controller. It is small, an advantage because of limited space in the laboratory, and contains the display, printer, and mass storage. The computer is interfaced to the automatic buret and the colorimeter. In addition to controlling the buret operation, the computer accepts data from the buret and colorimeter, treats the data to locate the end point, and outputs the results.

A rigid, fixed Teflon support holds the titrant delivery tube, stirring rod, and colorimeter probe. The sample cell is raised into position against the bottom of the support. To minimize the manipulations required of the analyst, the cell is raised by a pneumatic cylinder actuated by a manual switch.

The Metrohm 655 Dosimat was selected to deliver the titrant because it is capable of the required precision and is suitable for interfacing to the computer. The computer and buret are connected with a 16-bit GP-IO Interface which allows bidirectional information transfer. The computer controls all functions of the buret and can accept data from it.

The end point is determined photometrically using a dipping-probe colorimeter. The Brinkmann instrument is inexpensive and easily interfaced to the computer through a BCD interface. The photometric detection system measures the disappearance of the reduced form of the ferroin indicator using an interference filter monochromator at 520 nm. Light from the colorimeter passes through a fiber-optic light guide, through the sample solution, is reflected off a mirror back through the solution onto another fiber-optic bundle, and back to the colorimeter. Ambient light is not a problem. Light coming in at an angle is reflected out the other side. Only incident light perpendicular to the mirror from the source is reflected back into the entrance of the pickup bundle.

Precise location of the end point is critical to get good precision. It is desirable to titrate the samples as quickly as possible following reduction for increased throughput and to minimize air oxidation of the Pu(III). Titrant is added rapidly to near the end point and then the buret is switched to incremental addition. Increments of 0.01 mL are added, the absorbance measured after each addition and the values stored. To deliver this small volume, the delivery tip is immersed into the solution. A very small delivery tip is used to prevent backup of sample into the tube and diffusion of titrant into the sample. The break in the absorption curve is very sharp. Rather than attempt to stop at the end point, the titration is continued past the end point and the stored values used to locate the end point. Best precision is obtained by locating the end point as the intercept of two linear least squares fitted lines before and after the break in the titration curve of absorbance vs mL of titrant. The data points are not smoothed, but are used as measured. For the titration conditions established, six points before and after the break in the titration curve are used to calculate the two lines used to locate the end point.

Stirring is critical for good precision. The stirring needs to be fast to mix the titrant and bulk solution rapidly, but must avoid cavitation and splatter. We use a glass paddle stirring rod rotated at 1800 rpm. A close fitting hole in the Teflon support serves as a good bearing to prevent wobble and spattering. The stirring paddle is located adjacent to the tip of the probe colorimeter to assure that solution is swept through the optical path. The forceful action of the stirrer also serves to prevent gas bubbles from depositing on the walls of the colorimeter probe tip which could result in incorrect absorbance measurements.

Thermal expansion of the solution could cause the titer of ceric titrant to vary with temperature. A thermistor interfaced to the computer measures the temperature of the titrant and the titrant volume can be corrected before making the final calculations. For the few degrees change in temperature we have observed in our laboratory, no correction is necessary.

Programs have been developed for blank determination, ceric titrant standardization, and plutonium sample titration. The programs are stored on a cassette tape.

After loading into the computer, a menu offers choices of titration to perform. For a sample titration, the analyst enters the sample identification data and sample weight and initiates the titration. The automatic titrator calculates the approximate quantity of titrant required from the sample weight, rapidly adds 95% of the titrant, switches to incremental addition and titrates through the end point, calculates the end point, and outputs a paper tape print-out giving sample identification, titrant volume, and percent plutonium. Other data can be printed if desired. A real-time plot of absorbance vs titrant volume displayed on the HP-85 screen is useful for diagnostics. Total time required for titration of a 250-mg sample is less than 5 min. Precision of the titration is less than 0.03% relative standard deviation for a single determination at the 250-mg plutonium level comparable to the precision attainable by an experienced analyst with manual titration using a weight buret. The automatic titrator does not require a skilled analyst to attain this precision and analyst bias in locating the end point is eliminated.

We have developed a rapid, automatic titrator for high precision plutonium assay which improves the reliability of the determination and reduces the time required of the analyst.

REFERENCES

[1] CALDWELL, E. E., et al., Anal. Chem. 34, 346 (1962).

[2] ROST, G. A., Anal. Chem. 33, 736 (1961).